ture was heated at reflux for 2 hr after the addition was complete. The reaction mixture was cooled and filtered under a cone of N_2. The solvent was removed by distillation through a 10-cm Vigreux column at atmospheric pressure. The residue was then distilled. A central fraction of 57 g (72% yield), bp 130° (0.001 mm), was collected. Ir showed a C–C double bond at 1680 cm^{-1}; nmr s (18 H) δ 0.29, m (4 H) 1.4, m (4 H) 2.5, m (10 H) 7.48.

1,1-Diphenyl-5-hydroxy-1-sila-4-cycloheptanone. In a 300-ml round-bottom flask equipped with a magnetic stirring bar were placed 53 g (0.12 mol) of 1,1-diphenyl-4,5-bis(trimethylsiloxy)-1-sila-4-cycloheptene, 75 ml of THF, and 75 ml of 2 *N* HCl. The mixture was stirred overnight. The layers were separated. The organic layer was dried over anhydrous $MgSO_4$ and filtered and the solvent was evaporated. The yield of crystalline product was 35 g (95%), mp 94–97°. Recrystallization from *n*-hexane gave a white solid, mp 96–98°. Ir showed a broad OH band at 3450 cm^{-1} and a carbonyl band at 1710 cm^{-1}; nmr m (4 H) δ 1.45, m (2 H) 2.1, m (2 H) 2.65, broad s (1 H) 3.8, m (1 H) 4.25, m (10 H) 7.19. *Anal.* Calcd for $SiC_{18}H_{20}O_2$: C, 72.93; H, 6.80. Found: C, 72.73; H, 6.60.

1,1-Diphenyl-4,5-dihydroxy-1-silacycloheptane. In a dry 500-ml round-bottom three-necked flask equipped with a pressure-equalizing addition funnel, a magnetic stirring bar, and a reflux condenser was placed 3 g (0.075 mol) of $LiAlH_4$ in 100 ml of ether. In the addition funnel was placed 35.0 g (0.12 mol) of crude 1,1-diphenyl-5-hydroxy-1-sila-4-cycloheptanone in 100 ml of anhydrous THF. This solution was added to the hydride suspension at a rate to maintain reflux. After 2 hr the reaction was quenched by the addition of water. The layers were separated. The organic layer was dried over anhydrous $MgSO_4$ and filtered and the solvent was removed at reduced pressure, resulting in 33 g of a thick yellow oil which solidified on standing: nmr m (8 H) δ 1–2, m (4 H) 3.7, m (10 H) 7.3. Its ir showed two OH bands in CCl_4, one at 3300 cm^{-1} and the other at 3550 cm^{-1}.

1,1-Diphenyl-1-sila-4-cycloheptene. In a dry 50-ml flask equipped with a magnetic stirring bar were placed 1 g (3.4 mmol) of 1,1-diphenyl-1-sila-4,5-cycloheptanediol, 1.4 ml (10 mmol) of triethylamine, and 20 ml of CH_2Cl_2. The solution was cooled to 0° and 0.6 ml (7.5 mmol) of mesyl chloride was added.[25] The mixture was stirred for 2 hr and then poured into 50 ml of H_2O. The layers were separated. The organic layer was dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The crude dimesylate, 3.0 g (20 mmol) of NaI, and 20 ml of methyl ethyl ketone were placed in a 50-ml flask equipped with a reflux condenser and a magnetic stirring bar.[27] The solution was stirred at reflux for 40 hr; 50 ml of ether was added. The reaction mixture was washed with two 50-ml portions of water and once with a saturated solution of $Na_2S_2O_4$ to disperse the I_2 color. It was dried over anhydrous $MgSO_4$ and filtered and the solvents were removed at reduced pressure. The residue, 610 mg, was then chromatographed through a 10 × 0.5 in. alumina column with *n*-hexane. In this way 330 mg (37% yield) of crystalline olefin was collected. It was recrystallized from 95% ethanol, mp 63°.

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Registry No.—1,1-Dimethyl-1-sila-5-thiacyclooctane, 49592-51-0; dimethyldiallylsilane, 1113-12-8; H_2S, 7783-06-4; 1,1-dimethyl-1-sila-5-thiacyclooctane 5,5-dioxide, 51051-56-0; 1,1-dimethyl-1-sila-4-cycloheptene, 51051-57-1; 4,4-dimethyl-4-sila-6-heptene 1-thiolacetate, 51006-76-9; thiolacetic acid, 507-09-5; dimethylallyl-3-mercaptopropylsilane, 49592-52-1; 1,1-diphenyl-1-sila-5-thiacyclooctane, 51051-58-2; diphenyldiallylsilane, 10519-88-7; 1,1-diphenyl-1-sila-5-thiacyclooctane 5,5-dioxide, 51051-59-3; 1,1-diphenyl-1-sila-4-cycloheptene, 51051-60-6; 1,1-dimethyl-5-hydroxy-1-sila-4-cycloheptanone, 10325-25-4; 1,1-dimethyl-4,5-bis-(trimethylsiloxy)-1-sila-4-cycloheptene, 32297-03-3; *cis*-1,1-dimethyl-1-sila-4,5-cycloheptanediol, 51051-61-7; 1,1-diphenyl-4,5-bis(trimethylsiloxy)-1-sila-4-cycloheptene, 51051-62-8; dimethyl 4,4-diphenyl-4-sila-1,7-heptanedioate, 34564-74-4; 1,1-diphenyl-5-hydroxy-1-sila-4-cycloheptanone, 51051-63-9; 1,1-diphenyl-4,5-dihydroxy-1-silacycloheptane, 51051-64-0.

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Preparation of New Nitrogen-Bridged Heterocycles. Reaction of Pyridinium *N*-Imines with α-Haloacrylates in the Presence of Alkali

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Pyridinium *N*-imine hydriodides (**1–5**) reacted with ethyl and methyl α-chlorocinnamates and methyl α-bromocrotonate in the presence of alkali at room temperature to afford the corresponding 1,9a-dihydro-2*H*-pyrido[1,2-*b*]-*as*-triazine derivatives (**11–17**). Structural elucidation of these compounds was accomplished by physical and spectral means and by the conversion of compounds **11** and **16** to the dehydrogenated 2*H*-pyrido[1,2-*b*]-*as*-triazines **20** and **21**.

Pyridinium *N*-imine is a very useful and versatile precursor for preparations of various nitrogen-bridged heterocycles[1] and N-substituted iminopyridinium ylides[2] as described in many reports. In particular, increased attention

Table I
Nmr Spectral Data of Pyridotriazines

Compd[a]	NH[g]	C-2	C-6	C-7	C-8	C-9	C-9a	R″	R′	
11	2.00	*b*	6.53	*b*	1.72	*b*	*b*	7.16	4.13	1.27
	b		d		s			s	q	t
	$J_{6,7}$ = 7.0, J_{Et} = 7.0									
12	2.15	*c*	6.55	*c*	5.80	*c*	*c*	7.15	4.13	1.25
	b		dd		m			s	q	t
	$J_{6,7}$ = 7.0, $J_{6,8}$ = 1.5, J_{Et} = 7.0									
13	2.10	*d*	2.10	*d*	5.77	*d*	*d*	7.15	4.12	1.22
	b		s		m			s	q	t
	J_{Et} = 7.0									
14	1.96	*e*	6.49	*e*	5.64	*e*	*e*	7.16	4.19	1.27
	b		d		bd			s	q	t
	$J_{6,7}$ = 7.5, $J_{7,8}$ = 6.0, J_{Et} = 7.0									
15	1.80	4.75	6.36	1.68	5.53	1.68	4.85	7.15	4.13	1.28
	b	bd	bs	s	bs	s	bs	s	q	t
	J_{Et} = 7.0									
16	1.90	*f*	6.49	*f*	1.72	*f*		7.12	3.65	
	b		d		s			s	s	
	$J_{6,7}$ = 7.5									
17	1.65	3.65	6.47	4.72	1.77	5.00	5.21	1.26	3.69	
	b	m	d	dd	s	bs	bs	d	s	
	$J_{2,Me}$ = 6.0, $J_{6,7}$ = 7.0, $J_{7,9}$ = 1.5									
20		5.57	6.97	5.50	2.00	6.13		7.10	4.17	1.29
		s	d	dd	s	bs		s	q	t
	$J_{6,7}$ = 7.5, $J_{7,9}$ = 2.0, J_{Et} = 7.0									
21		5.62	7.02	5.56	2.04	6.17		7.15	3.75	
		s	d	dd	s	bs		s	s	
	$J_{6,7}$ = 7.5, $J_{7,9}$ = 2.0									

[a] All compounds were measured in carbon tetrachloride. [b] Overlapped with each other in the range of δ 4.6–5.1. [c] Overlapped with each other in the range of δ 4.6–5.3. [d] Overlapped with each other in the range of δ 4.6–5.3. [e] Overlapped with each other in the range of δ 4.6–5.3. [f] Overlapped with each other in the range of δ 4.6–5.4. [g] Exchanged with deuterium oxide.

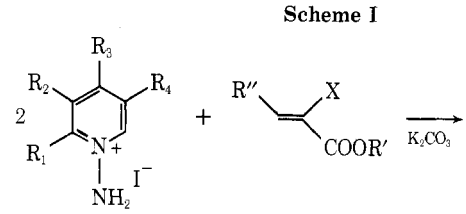
has been paid to the nitrogen-bridged heterocycles in recent years, since their preparations by other methods are difficult.

We recently reported that reactions of pyridinium *N*-imines with β-haloacrylates gave mainly 1,5-dipolar *N*-vinyliminopyridinium ylides, which react intramolecularly to give dihydropyrazolopyridines[3] and intermolecularly with acetylenic compounds to give *N*-dienyliminopyridinium ylide and vinylpyridine derivatives.[4] In continuation of this work, we attempted to carry out the reaction of pyridinium *N*-imines with some α-haloacrylates in the presence of alkali and have found a one-step preparative method for the novel 1,9a-dihydro-2*H*-pyrido[1,2-*b*]-*as*-triazines.

Results and Discussion

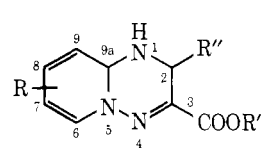
Reactions of Pyridinium *N*-Imine Hydriodides (1–5) with α-Haloacrylates in the Presence of Alkali. A 2:1 mixture of pyridinium *N*-imine hydriodide (**1**) and ethyl α-chlorocinnamate was treated with potassium carbonate in chloroform at room temperature for 4 days to give a yellow, crystalline product (**11**) in 84% yield, together with considerable amounts of γ-picoline. Similar products (**12–15**) were obtained by the reactions of the hydriodides **2–5** with the same reagent in yields of 4–87%. Reactions of the hydriodide **1** with methyl α-chlorocinnamate and methyl α-bromocrotonate gave compounds **16** and **17** in 85 and 36% yields. With hydriodides **1** and **2**, 1,3-dipolar cycloadducts **18** and **19** were also obtained in 5 and 38% yields. In these reactions no ylidic compound could be detected. These results are shown in Scheme I.

Scheme I



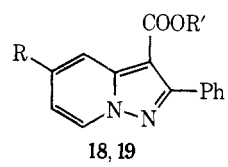
1–5

	R_1	R_2	R_3	R_4
1	H	H	Me	H
2	H	H	H	H
3	Me	H	H	H
4	H	Me	H	H
5	H	Me	H	Me



11–17

	R′	R″	C_6	C_7	C_8	C_9
11	Et	Ph	H	H	Me	H
12	Et	Ph	H	H	H	H
13	Et	Ph	Me	H	H	H
14	Et	Ph	H	H	H	Me
15	Et	Ph	H	Me	H	Me
16	Me	Ph	H	H	Me	H
17	Me	Me	H	H	Me	H

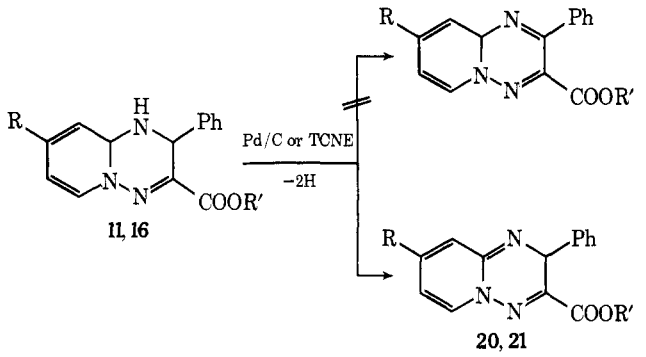


18, 19

	R	R′
18	Me	Et
19	H	Et

The products **11–17** were very stable under neutral and basic conditions, but were unstable in acid. The ir spectra showed characteristic absorption bands of a secondary amino group at 3290–3330 cm^{-1} and of an α,β-unsaturated carbonyl group at 1695–1713 cm^{-1}, respectively. The nmr spectrum (Table I) of compound **17**, for example, exhibited signals[6] at δ 6.47 (1 H, d), 5.21 (1 H, bs), 5.00 (1 H, bs), 4.72 (1 H, dd), and 1.77 (3 H, s) due to a dihydropyridine moiety and at δ 3.65 (1 H, m), 1.26 (3 H, d), 3.69 (3 H, S), and 1.65 (1 H, b) attributable to the residual skeleton. The signal at δ 1.65 (1 H, b) was exchanged with deuterium oxide (active amino proton) and the signals at δ

Scheme II



R R'
11 Me Et 20
16 Me Me 21

5.21 (1 H, bs) and 3.65 (1 H, m) were sharpened, indicative of their adjacent situation with the amino group. From these data the compounds **11–17** were assigned to be 1,9a-dihydro-2*H*-pyrido[1,2-*b*]-*as*-triazine derivatives.

To obtain further evidence for the proposed structure, we attempted the dehydrogenation of the compounds **11** and **16** to the corresponding pyridotriazine derivatives. Treatment of compounds **11** and **16** with lead tetraacetate gave intractable, tarry materials, but with palladium on carbon or tetracyanoethylene, the expected pyrido[1,2-*b*]-*as*-triazines **20** and **21** were obtained in low yields (Scheme II).

The ir spectrum of the compound **20** showed no absorption at the amino absorption region but a new band at 1660 cm^{-1} due to an unsaturated bond was present, and the nmr signals attributable to a bridgehead proton and an amino proton were absent. The large downfield shifts of the protons on the pyridine ring suggested that these compounds were not the 9a*H*-pyrido[1,2-*b*]-*as*-triazine derivatives but the alternative 2*H* isomers. Similar correlation of the chemical shifts was observed between 3,3a-dihydropyrazolopyridines[3,4] and 2,3-dihydroindolizines[7] described in our previous papers. The nmr data of pyridotriazine derivatives **11–17**, **20** and **21** are summarized in Table I.

In contrast with the stability of the dihydro compounds **11–17**, the pyridotriazines **20** and **21** were unstable and decomposed gradually even at room temperature.[5]

Reaction Mechanism. Tentative mechanisms for these reactions are shown in Scheme III.

The reactions may be initiated by Michael addition of pyridinium *N*-imine to the α-haloacrylate followed by elimination of pyridine derivative. Nucleophilic substitution of another molecule of the *N*-imine to the resulting haloaziridine **23** (path a) or nucleophilic addition to the azirine **24** (path b) would lead to the *N*-(2-aziridinyl)iminopyridinium ylide **25**, which rearranges to dihydropyridotriazine *via* the 1,6-dipolar intermediate **26**. The alternative course (path c) was negligible, since the product expected from the reaction *via* the 1,3-dipolar species **27** is a different type of dihydropyridotriazine (**29** and/or **30**). Nucleophilic substitution of haloaziridine has been reported by Deyrup and Greenwald[8] but the addition of pyridinium *N*-imidine to the carbon–nitrogen double bond is unknown. Pyridinium *N*-imine also reacted with dimethyl maleate to give dimethyl aminofumarate; this reaction should proceed *via* Michael addition of the *N*-imine to the α,β-unsaturated ester.[9] An attempt to obtain a pyridopyridazine from pyridinium *N*-imine and halocyclopropane[10] was unsuccessful.[11]

Experimental Section

Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer 240 Elemental Analyzer. The nmr spectra were determined with a JEOL JNM-4H-100 spectrometer in carbon tetrachloride with tetramethylsilane as an internal standard. The chemical shifts are expressed in δ values. The ir spectra were taken with a JASCO DS-301 spectrophotometer.

Reactions of Pyridinium *N*-Imine Hydriodides (1–5) with α-Haloacrylates in the Presence of Alkali. General Method. A mixture of pyridinium *N*-imine hydriodide (2 mmol) and α-haloacrylate (1 mmol) was treated with potassium carbonate (10 g) in chloroform at room temperature for 4–8 days. The reaction mix-

Scheme III

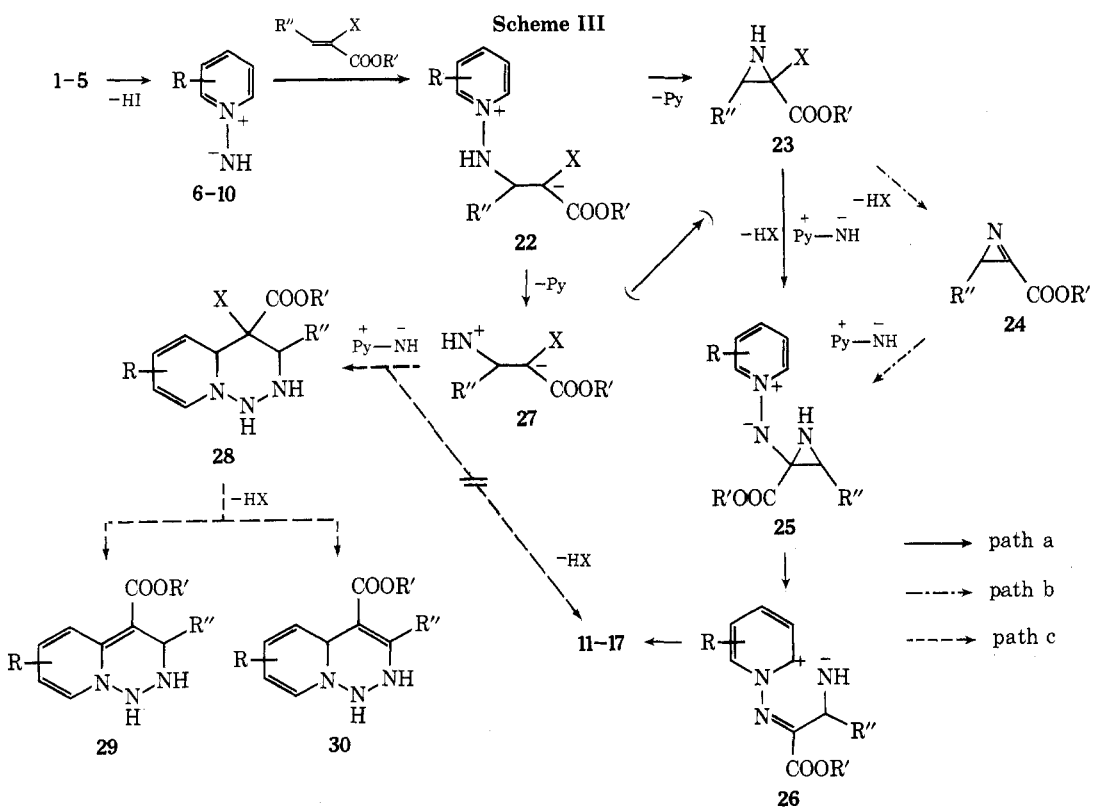


Table II
Results and Some Properties of Dihydropyridotriazines

Compd[b]	Reactant: *N*-Imine	Reactant: α-Haloacrylate[a]	Yield, %	Mp, °C	Ir (KBr), cm⁻¹: C=O	Ir (KBr), cm⁻¹: NH
11	**1**	ECC	84	112–115	1710	3330
12	**2**	ECC	4	125–127	1700	3310
13	**3**	ECC	27	91–93	1713	3290
14[c]	**4**	ECC	64	136–139	1695	3320
15	**5**	ECC	87	106–109	1695	3290
16	**1**	MCC	85	143–145	1717	3320
17	**1**	MBC	36	74–76	1708	3290

[a] ECC, ethyl chlorocinnamate; MCC, methyl chlorocinnamate; MBC, methyl bromocrotonate. [b] **11**. *Anal.* Calcd for $C_{17}H_{19}N_3O_2$: C, 68.66; H, 6.44; N, 14.13. Found: C, 68.92; H, 6.45; N, 13.92. **12**. Calcd for $C_{16}H_{17}N_3O_2$: C, 67.82; H, 6.05; N, 14.83. Found: C, 67.75; H, 6.15; N, 14.70. **13**. Calcd for $C_{17}H_{19}N_3O_2$: C, 68.66; H, 6.44; N, 14.13. Found: C, 68.89; H, 6.55; N, 13.79. **14**. Calcd for $C_{17}H_{19}N_3O_2$: C, 68.66; H, 6.44; N, 14.13. Found: C, 68.62; H, 6.53; N, 13.87. **15**. Calcd for $C_{18}H_{21}N_3O_2$: C, 69.43; H, 6.80; N, 13.50. Found: C, 69.39; H, 6.91; N, 13.20. **16**. Calcd for $C_{16}H_{17}N_3O_2$: C, 67.82; H, 6.05; N, 14.83. Found: C, 67.99; H, 6.17; N, 14.83. **17**. Calcd for $C_{11}H_{15}N_3O_2$: C,59.71; H, 6.83; N, 18.99. Found: C, 59.90; H, 6.85, N, 18.81. [c] The 7-methyl isomer could not be detected.

ture was filtered to remove insoluble inorganic substances and the filtrate was concentrated under reduced pressure. The residual oil was separated by column chromatography (alumina) using ether as an eluent. Recrystallization from ether–*n*-hexane gave the corresponding 1,9a-dihydro-2*H*-pyrido[1,2-*b*]-*as*-triazine derivatives as yellow crystals. In these reactions considerable amounts of the corresponding pyridine derivatives were formed, which could be detected by thin layer chromatography and their odor. In the cases of the hydriodides **1** and **2** with ethyl α-chlorocinnamate the corresponding pyrazolo[1,5-*a*]pyridine derivatives **18** and **19** were also obtained in 5 and 38% yields. The structures of these compounds (**18** and **19**) were determined by the spectral comparisons with the methyl ester derivatives prepared by the reactions of pyridinium *N*-imines **6** and **7** with methyl phenylpropiolate. These results and some properties of these dihydropyridotriazine derivatives (**11**–**17**) are listed in Table II.

3-Ethoxycarbonyl-5-methyl-2-phenylpyrazolo[1,5-*a*]pyridine (**18**) was obtained as colorless needles (from ether–*n*-hexane): mp 88–90°; $\nu_{C=O}$ (KBr) 1719 cm⁻¹; nmr (CCl_4) δ 1.22 (3 H, t, J = 7.0 Hz, OCH_2CH_3), 2.41 (3 H, s, C_5 CH_3), 4.17 (2 H, q, J = 7.0 Hz, OCH_2CH_3), 6.55 (1 H, dd, J = 7.5, 1.0 Hz, C_6 H), 7.25 (3 H, m, meta and para protons of C_2 phenyl), 7.62 (2 H, m, ortho protons of C_2 phenyl), 7.84 (1 H, bs, C_4 H), and 8.20 (1 H, d, J = 7.5 Hz, C_7 H).

Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.84; H, 5.78; N, 9.68.

3-Ethoxycarbonyl-2-phenylpyrazolo[1,5-*a*]pyridine (**19**) was obtained as colorless needles (from ether–*n*-hexane): mp 73–75°; $\nu_{C=O}$ (KBr) 1718 cm⁻¹; nmr (CCl_4) δ 1.25 (3 H, t, J = 7.0 Hz, OCH_2CH_3), 4.19 (2 H, q, J = 7.0 Hz, OCH_2CH_3), 6.73 (1 H, t, J = 7.0, 7.0 Hz, C_6 H), 7.20 (1 H, bt, J = 7.0, 8.0 Hz, C_5 H), 7.29 (3 H, m, meta and para protons of C_2 phenyl), 7.67 (2 H, m, ortho protons of C_2 phenyl), 8.10 (1 H, dd, J = 8.0, 1.0 Hz, C_4 H), and 8.37 (1 H, d, J = 7.0 Hz, C_7 H).

Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.40; H, 5.33; N, 10.30.

Dehydrogenation of Dihydropyridotriazines (11 and 16). General Method. A. A mixture of dihydropyridotriazine (200 mg) and palladium on carbon (5%, 1.0 g) was stirred in dry benzene (30 ml) at room temperature for 4 days. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was separated by column chromatography (alumina) using methylene chloride as an eluent. From this procedure 2*H*-pyridotriazine derivatives **20** and **21** were obtained in 30 and 25% yields, respectively.

B. A equimolar mixture of dihydropyridotriazine and tetracyanoethylene was stirred in dry benzene at room temperature for 1 day. Similar treatment of the reaction solution gave 2*H*-pyridotriazine derivative. The yields of the compounds **20** and **21** were 50 and 45%.

3-Ethoxycarbonyl-8-methyl-2-phenyl-2*H*-pyrido[1,2-*b*]-*as*-triazine (**20**) was obtained as orange crystals (from chloroform–*n*-hexane), mp 108–110°, ν (KBr) 1713 (C=O) and 1660 cm⁻¹ (C=N); its picrate, yellow crystals (from ethanol), had mp 178–181° dec, $\nu_{C=O}$ (KBr) 1736 cm⁻¹.

Anal. Calcd for $C_{23}H_{20}N_6O_9$: C, 52.67; H, 3.84; N, 16.03. Found: C, 52.88; H, 3.82; N, 15.74.

3-Methoxycarbonyl-8-methyl-2-phenyl-2*H*-pyrido[1,2-*b*]-*as*-triazine (**21**) was an amorphous substance; its picrate, yellow crystals (from ethanol), had mp 189–192° dec, $\nu_{C=O}$ (KBr) 1740 cm⁻¹.

Anal. Calcd for $C_{22}H_{18}N_6O_9$: C, 51.77; H, 3.55; N, 16.47. Found: C, 51.65; H, 3.50; N, 16.40.

Reaction of Pyridinium *N*-Imine (6) with Dimethyl Maleate. A mixture of pyridinium *N*-imine hydriodide (**1**, 0.24 g, 1 mmol) and dimethyl maleate (0.14 g, 1 mmol) was treated with potassium carbonate (5 g) in chloroform at room temperature for 4 days. The reaction mixture was worked up by the procedure described above to give dimethyl aminofumarate in 35% yield as a colorless oil. The structure of this product was determined by comparison with an authentic specimen.[9] The reaction of the hydriodide **1** with ethyl cinnamate was unsuccessful.

Registry No.—**1**, 7583-92-8; **2**, 6295-87-0; **3**, 7583-90-6; **4**, 7583-91-7; **5**, 7585-71-9; **11**, 51065-68-0; **12**, 51065-69-1; **13**, 51065-70-4; **14**, 51065-71-5; **15**, 51065-72-6; **16**, 51065-73-7; **17**, 51065-74-8; **18**, 51065-75-9; **19**, 51065-76-0; **20**, 51065-77-1; **20** picrate, 51065-78-2; **21**, 51065-79-3; **21** picrate, 51065-80-6; ECC, 26880-33-1; MCC, 4519-51-1; MBC, 17642-18-1; dimethyl maleate, 624-48-6.

References and Notes

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